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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a nonaqueous secondary battery.

[0002]

[Description of the Prior Art]Consist of a cathode, an anode, and nonaqueous electrolyte and by charge the nonaqueous secondary battery in which repeated use is possible, From having a high energy density compared with aqueous solution system rechargeable batteries, such as a lead storage battery and a nickel-cadmium battery, research is actively done as a power supply of a noncommercial cellular phone, a portable device, a Personal Digital Assistant, etc.

[0003]The cathode containing the positive active material which can carry out an electrochemical reaction reversibly with a lithium ion among said nonaqueous secondary batteries, Research is actively done from the lithium ion battery which consists of an anode which contains reversibly occlusion and the negative electrode active material which may be emitted for a lithium ion, and nonaqueous electrolyte containing lithium salt being provided with high tension, high energy density, the outstanding cycle life, high safety, etc.

[0004] Generally as said nonaqueous electrolyte, high dielectric constant solvents, such as ethylene carbonate and propylene carbonate, What dissolved supporting electrolytes, such as LiPF_6 and LiBF_4 , in the mixed solvent with low viscosity solvents, such as dimethyl carbonate and diethyl carbonate, is used.

[0005]The outstanding elevated-temperature neglect characteristic is called for in said nonaqueous secondary battery. Said nonaqueous secondary battery with which this is used for the cellular phone neglected by automatic in the train [by which outdoor parking was carried out] at the daytime of midsummer, for example is because it may be exposed to the hot environments which deviated from anticipated-use environment.

[0006]However, when said nonaqueous electrolyte was the above composition and elevated-temperature neglect of the cell of a charging state was carried out, there was a problem that a high temperature conservation characteristic fell -- a cell blisters or service capacity falls.

[0007]Since the cell was neglected under hot environments, it is considered to be because for a gas to occur [that the steam pressure of the electrolysis solution rose, and] when an electrolysis solution decomposes on an electrode that a cell blisters as mentioned above. Among these, about generating of the gas on an electrode. For example, in the case of the solvent of the two-component system of EC and EMC, below 70 **, generating of methane in an anode, etc. is the main causes, and becoming the main causes understands

generating of the carbon dioxide in a cathode from our old examination, so that temperature becomes high exceeding 70 °C.

[0008] It is thought that it is based on the rise of the decomposition reaction of the electrolysis solution on a cathode and an anode and the reaction resistance of an electrode, decline in the conductivity of an electrolysis solution, blinding of a separator, the inter-electrode crevice increase resulting from bulging of a cell, etc. that service capacity falls as mentioned above.

[0009] The fall of said elevated-temperature neglect characteristics, such as bulging of a cell and reduction of residual service capacity, is so intense that leaving times is so long that neglect temperature is high.

[0010]

[Problem to be solved by the invention] It was completed based on the above situations and this invention is ****. The purpose is to provide the nonaqueous secondary battery provided with the elevated-temperature neglect characteristic.

[0011]

[The means for solving a technical problem, and an operation and an effect] As a means for attaining the above-mentioned purpose, invention of Claim 1, In the nonaqueous secondary battery which consists of a cathode, an anode, and nonaqueous electrolyte, that it is few as said nonaqueous electrolyte is chosen from a sultone compound, cyclic sulfate, and vinylene carbonate A kind, It is characterized by the thing which is chosen from the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group and which contain a kind at least.

[0012] The elevated-temperature neglect characteristic in 70 °C or less improves by [which contain a kind at least] choosing nonaqueous electrolyte from a sultone compound, cyclic sulfate, and vinylene carbonate.

This is considered to be based on the following Reasons. If the above-mentioned compound is contained in an electrolysis solution, when said compound decomposes on an anode, a film will be formed on an anode. Generating of the methane etc. which originate in disassembly of the electrolysis solution on an anode and disassembly of the electrolysis solution selectively disassembled on the cathode by the film concerned can be controlled.

[0013] On the other hand, the elevated-temperature neglect characteristic in the temperature region over 70 °C improves by [which contain a kind at least] choosing nonaqueous electrolyte from the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group. This is considered to be based on the following Reasons. If the above-mentioned compound is contained in an electrolysis solution, when said compound decomposes and polymerizes on a cathode, a film will be formed on a cathode. Generating of the carbon dioxide etc. which originate in disassembly of the electrolysis solution on a cathode and disassembly of the electrolysis solution selectively disassembled on the anode by the film concerned can be controlled.

[0014] That it is few as nonaqueous electrolyte is chosen from a sultone compound, cyclic sulfate, and vinylene carbonate And a kind, Compared with the case where the above-mentioned compound is used alone, respectively, the elevated-temperature neglect characteristic improves by [which contain a kind at least] being chosen out of the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group. This is considered to be based on the following Reasons.

[0015]When not using the above-mentioned compound at all, on the electrode set under hot environments, disassembly of an electrolysis solution advances and gas [, such as carbon dioxide,], such as methane, is emitted with the temperature. At this time, not only an electrolysis solution but the electrolysis solution selectively disassembled on the electrode of another side is considered to both be decomposed on an electrode.

[0016]Namely, also in the case where formed the film on the anode in a temperature zone 70 ° or less, and the generation of gas on an anode is controlled, Also in the case where became the cause of generating carbon dioxide etc. when the electrolysis solution selectively disassembled with the anode decomposes with a cathode, formed the film on the cathode in the temperature zone over 70 °, and the generation of gas on a cathode is controlled, When the electrolysis solution selectively disassembled with the cathode decomposes with an anode, it becomes the cause of generating methane etc.

[0017]That it is few as nonaqueous electrolyte is chosen from a sultone compound, cyclic sulfate, and vinylene carbonate And a kind, Disassembly of the electrolysis solution in the electrode in which the film was formed can be controlled by [which contain a kind at least] being chosen out of the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group. It does not become impossible to accept it but it can also control that the electrolysis solution disassembled selectively is disassembled further on the other poles. As a result, the case which contained only a kind at least where it is chosen out of a sultone compound, cyclic sulfate, and vinylene carbonate, Compared with the case which contained only a kind at least where it is chosen out of the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group, more than it added both performance, the elevated-temperature neglect characteristic improves.

[0018]As for the addition of the compound chosen from a sultone compound, cyclic sulfate, and vinylene carbonate, in order to control disassembly of an electrolysis solution effectively, without reducing the initial service capacity on the anode under hot environments, 5 or less weight % of 0.1 weight % or more is preferred to the total amount of electrolysis solutions. In particular, 2 or less weight % of 0.5 weight % or more is preferred.

[0019]The addition of the compound chosen from the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group, In order to control effectively disassembly of the electrolysis solution on the cathode under hot environments, 4 or less weight % of 2 weight % or more is preferred to the total amount of electrolysis solutions.

[0020]Invention of Claim 2 is characterized by said sultone compound being butane propane sultone, a propene sultone, or a sultone in an invention described in Claim 1.

[0021]Since the film stabilized on the anode by using the above-mentioned substance as said sultone compound can be formed, the elevated-temperature neglect characteristic improves.

[0022]Invention of Claim 3 is characterized by said cyclic sulfate being propylene glycol either glycol sulfate or sulfate in the thing according to claim 1 or 2.

[0023]Since the film stabilized on the anode by using the above-mentioned substance as said cyclic sulfate can be formed, the elevated-temperature neglect characteristic improves.

[0024]In the thing according to any one of claims 1 to 3 invention of Claim 4, The alkylbenzene derivative which has the third class carbon which adjoins said phenyl group, It is characterized by being 1,4-bis(1-

methylpropyl)a cumene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, 1-methylpropyl benzene, 1,3-bis (1-methylpropyl)benzene, or benzene.

[0025]Since the film stabilized on the cathode by using the above-mentioned substance as an alkylbenzene derivative which has the third class carbon which adjoins said phenyl group can be formed, the elevated-temperature neglect characteristic improves.

[0026]Invention of Claim 5 is characterized by said cycloalkyl benzene derivative being cyclopentylether cyclohexylbenzene or benzene in the thing according to any one of claims 1 to 4.

[0027]Since the film stabilized on the cathode by using the above-mentioned substance as said cycloalkyl benzene derivative can be formed, the elevated-temperature neglect characteristic improves.

[0028]Invention of Claim 6 is characterized by said biphenyl derivative being 2-chlorobiphenyl, 2-fluorobiphenyl, 2-bromobiphenyl, or biphenyl in the thing according to any one of claims 1 to 5.

[0029]Since the film stabilized on the cathode by using the above-mentioned substance as said biphenyl derivative is formed, the elevated-temperature neglect characteristic improves.

[0030]

[Mode for carrying out the invention]Hereafter, the embodiment of this invention is described based on an accompanying drawing. Drawing 1 is an outline sectional view of the square-shaped nonaqueous secondary battery which is one embodiment of this invention. The cathode 3 in which this square-shaped nonaqueous secondary battery 1 applies positive electrode mixture to the positive pole collector which consists of aluminium foil, It is a thing with a 30 mm[in width] x48-mm thickness of 4 mm which stores the flat volume-like electrode group 2 by which the anode 4 which applies negative electrode mixture was wound around the negative pole collector which consists of copper foil via the separator 5, and nonaqueous electrolyte to the cell case 6. [in height]

[0031]The battery lid 7 which formed the safety valve 8 is attached to the cell case 6 by laser welding, the negative pole terminal 9 is connected with the anode 4 via the negative electrode lead 11, and the cathode 3 is connected with the battery lid via the positive electrode lead 10.

[0032]As a nonaqueous solvent of the nonaqueous electrolyte concerning this invention, For example, cyclic carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate. Chain carbonate, such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate. Cyclic ester, such as gamma-butyrolactone and gamma-valerolactone, methyl acetate, Chain ester species, such as methyl propionate, a tetrahydrofuran, 2-methyltetrahydrofuran, Chain ether, such as cyclic ether, such as tetrahydropyran, dimethoxyethane, and dimethoxymethane, The halogenide of chain phosphoric ester, such as cyclic-phosphoric-acid ester, such as phosphoric acid ethylene methyl and phosphoric acid ethylethylene, trimethyl phosphate, and phosphoric acid triethyl, and these compounds, etc. can be used. Only one kind may be chosen and used for these organic solvents, and may be used for them combining two or more kinds.

[0033]As a solute of the nonaqueous electrolyte concerning this invention, LiClO_4 , LiPF_6 , Inorganic lithium salt and LiCF_3SO_3 , such as LiBF_4 , Fluorine-containing organicity lithium salt, such as $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{CO})_2$, and $\text{Li}(\text{CF}_3\text{SO}_2)_3$, etc. can be mentioned. Only one kind may be chosen and used for these solutes, and may be used for them combining two or more kinds.

[0034]As a sultone compound added to nonaqueous electrolyte concerning this invention, it can choose from butanea propane sultone, a propene sultone, or a sultone, and can use.

[0035]As cyclic sulfate added to an electrolysis solution concerning this invention, it can choose from propylene glycol either glycol sulfate or sulfate, and can use.

[0036]Vinylene carbonate can be added to nonaqueous electrolyte concerning this invention. As an alkylbenzene derivative which has the third class carbon which adjoins a phenyl group added to nonaqueous electrolyte, Either which is chosen from a cumene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, 1-methylpropyl benzene, 1,3-bis(1-methylpropyl)benzene, and 1,4-bis(1-methylpropyl)benzene can be used.

[0037]Either which is chosen from cyclohexylbenzene and cyclopentylbenzene can be used as a cycloalkyl benzene derivative added to nonaqueous electrolyte concerning this invention.

[0038]As a biphenyl derivative added to nonaqueous electrolyte concerning this invention, either which is chosen from biphenyl, 2-fluorobiphenyl, 2-bromobiphenyl, and 2-chlorobiphenyl can be used. 2-fluorobiphenyl, 2-bromobiphenyl, and 2-chlorobiphenyl are more preferred, and especially 2-fluorobiphenyl is [among these] still more preferred.

[0039]As a separator, polymer porous membrane, such as polyethylene, polypropylene, and polyester, a nonwoven fabric, nonwoven fabrics, such as glass fiber, the nonwoven fabric of glass fiber and a polymer fiber, etc. can be used.

[0040]As positive active material, the lithium transition metal multiple oxide expressed with general formula LiMO_2 (M is a transition metal) which has stratified halite structure, and the lithium manganese multiple oxide which has Spinel structure can be used. The metal chalcogen ghost which does not contain lithium, such as TiO_2 , TiS_2 , V_2O_5 , MnO_2 , and MoO_3 , can be used. However, when using said metal chalcogen ghost, what is changed into the state where discharged such positive active material fully beforehand, or discharged selectively, and the lithium ion was doped is desirable.

[0041]The kind in particular of conducting agent may not be restricted, may be metal, or may be nonmetallic. As a metal conducting agent, the material which comprises metallic elements, such as Cu and nickel, can be mentioned. As a nonmetallic conducting agent, carbon materials, such as graphite, carbon black, acetylene black, and Ketchen black, can be mentioned.

[0042]If a binding agent is a stable material to the solvent and electrolysis solution which are used at the time of electrode manufacture, the kind in particular will not be restricted. Specifically Polyethylene, polypropylene, polyethylene terephthalate, Resin system polymers, such as aromatic polyamide and cellulose, a styrene butadiene rubber, Rubber-like polymers, such as polyisoprene rubber, butadiene rubber, and ethylene-propylene rubber, Styrene butadiene styrene block copolymer and its hydrogenation thing, Styrene ethylene-butadiene styrene block copolymer and its hydrogenation thing, Thermoplastic-elastomer-like polymers, such as styrene isoprene styrene block copolymer and its hydrogenation thing, Syndiotactic 1,2-polybutadiene, an ethylene-vinylacetate copolymer, Fluorine system polymers, such as elasticity resin-like polymers, such as a propylene-alpha olefin (carbon numbers 2-12) copolymer, polyvinylidene fluoride, polytetrafluoroethylene, and a polytetrafluoroethylene ethylenic copolymer, etc. can be used.

[0043]Polymer Compounds Sub-Division which has alkali-metal-ion conductivity, such as a lithium ion, can also be used especially as a binding agent. As a polymer which has such ion conductivity, Polyether system high molecular compounds, such as polyethylene oxide and polypropylene oxide, The crosslinked polymer compound of polyether, polyepichlorohydrin, polyphosphazene, A polysiloxane, a polyvinyl pyrrolidone,

polyvinylidene carbonate, The system which compounded the alkaline metal salt which makes lithium salt or lithium a subject with high molecular compounds, such as polyacrylonitrile, or the system which blended with this the organic compound which has high dielectric constants, such as propylene carbonate, ethylene carbonate, and gamma-butyrolactone, can be used. Such materials may be combined and used.

[0044]In a positive pole collector, aluminum, Ta, Nb, Ti, Hf, Zr, Zn, W, Bi, the alloy containing these metal, etc. can be illustrated, for example. These metal forms a passive state film in the surface by anodization in an electrolysis solution. Therefore, nonaqueous electrolyte can be effectively prevented from carrying out oxidative degradation in the liquid contact portion of a positive pole collector and an electrolysis solution. As a result, the cycle characteristic of a nonaqueous secondary battery can be improved effectively. The alloy which contains aluminum, Ti, Ta, and these metal among the above-mentioned metal can be used conveniently. Since especially aluminum and its alloy are lower density, they can make mass of a positive pole collector small compared with the case where other metal is used. Therefore, since the energy density of a cell can be raised, it is especially desirable.

[0045]When applying to a positive pole collector the positive electrode mixture produced by performing it above, a publicly known means can perform. When a mixture is slurry form, it can apply on a charge collector, for example using a doctor blade etc. When a mixture is paste state, it can apply on a charge collector, for example by roller coating etc. When the solvent is being used, an electrode can be produced by drying and removing a solvent.

[0046]The lithium aluminum alloy which is a substance **** and can emit a lithium metal and lithium as negative electrode active material, Lithium nitrides, such as lithium alloys, such as a lithium lead alloy and a lithium tin alloy, and Li_5 (Li_3N), Transition metal oxides, such as carbon materials, such as black lead, corks, and an organic matter baking body, WO_2 , MoO_2 , SnO_2 , SnO , TiO_2 , and NbO_3 , can be used. Only one kind may be chosen and used for such negative electrode active material, and may be used for it combining two or more kinds.

[0047]It is preferred that it is metal, such as copper, nickel, and stainless steel, and in these, it is easy to process the construction material of a negative pole collector into a thin film, since it is inexpensive, copper foil is used for it, but it is more preferred.

[0048]The manufacturing method in particular of an anode is not restricted, but can be manufactured by the manufacturing method of the above-mentioned cathode, and the same method.

[0049]Hereafter, this invention is explained in detail based on an working example. This invention is not limited at all by the following working example.

[0050]Polyvinylidene fluoride 8 weight section whose <working-example 1> cathode board is a binding agent, To the positive electrode mixture which mixes acetylene black 5 weight section which is a conducting agent, and lithium cobalt multiple oxide 87 weight section which is positive active material. After adding N-methyl pyrrolidone suitably and preparing to paste state, it manufactured by applying this to both sides of a 20-micrometer-thick aluminium foil charge collector, and drying.

[0051]The negative electrode plate was manufactured by applying this on a 15-micrometer-thick copper foil charge collector, and drying to the negative electrode mixture which mixes 2 weight % of carboxymethyl cellulose, and 3 weight % of styrene butadiene rubber with 95 weight % of graphite (black lead), after adding water suitably and preparing it to paste state.

[0052]The fine porous membrane made from polyethylene was used for the separator. To the mixed solvent which mixed ethylene carbonate and ethyl methyl carbonate at a rate of 3:7 by the volume ratio to the electrolysis solution, carry out 1 mol/l dissolution of the LiPF_6 , and to the total amount of electrolysis solutions 0.5 weight % of propane sultones, What added 3 weight % of cyclohexylbenzenes was used.

[0053]Twelve cells of nonaqueous secondary batteries with a 30 mm[in width] x48-mm thickness of 4 mm were produced using the above-mentioned component. [in height]

[0054>About the nonaqueous secondary battery of the working examples 2 thru/or 66 and the <comparative example 1 thru/or 13> working examples 2 thru/or 18. Twelve every cells each of nonaqueous secondary batteries were produced like the working example 1 except having added the substance which was replaced with a propane sultone and cyclohexylbenzene and was shown in Table 1 as a substance added to an electrolysis solution.

[0055>About the nonaqueous secondary battery of the working example 19 thru/or the working example 30, 12 every cells each of nonaqueous secondary batteries were produced like the working example 1 except having added the substance which was replaced with a propane sultone and cyclohexylbenzene and was shown in Table 2 as a substance added to an electrolysis solution.

[0056>About the nonaqueous secondary battery of the working example 31 thru/or the working example 48, 12 every cells each of nonaqueous secondary batteries were produced like the working example 1 except having added the substance which was replaced with a propane sultone and cyclohexylbenzene and was shown in Table 3 as a substance added to an electrolysis solution.

[0057>About the nonaqueous secondary battery of the working example 49 thru/or the working example 66, 12 every cells each of nonaqueous secondary batteries were produced like the working example 1 except having added the substance which was replaced with a propane sultone and cyclohexylbenzene and was shown in Table 4 as a substance added to an electrolysis solution.

[0058>About the nonaqueous secondary battery of the comparative example 1 thru/or the comparative example 17, 12 every cells each of nonaqueous secondary batteries were produced like the working example 1 except having added the substance which was replaced with a propane sultone and cyclohexylbenzene and was shown in Table 5 as a substance added to an electrolysis solution.

[0059]In [nonaqueous secondary battery / of the <measurement> (service capacity) working examples 1 thru/or 66 and the comparative examples 1 thru/or 17] 25 **, After charging for 3 hours by 600 mA of charging current, and the constant current-constant potential charge of the charge voltages 4.20V, service capacity when discharged on condition of 600 mA of discharge current and the final voltage 2.75V was measured, and this was made into initial service capacity.

[0060](Elevated-temperature shelf test) In 25 **, it charged for 3 hours by 600 mA of charging current, and the constant current-constant potential charge of the charge voltages 4.20V about the nonaqueous secondary battery of the working examples 1 thru/or 66 and the comparative examples 1 thru/or 17. Thus, cell thickness was measured after neglecting the cell made into the charging state at 100 ** for 48 hours. After neglecting the cell made into said charging state for 30 days at 60 **, cell thickness and service capacity were measured.

[0061]After said 60 ** neglect, once discharging, service capacity which carried out charge and discharge again and was measured was ** (ed) with said initial service capacity, and the capacitance retention (%) after 60 ** neglect was computed by multiplying this by 100.

[0062] The above-mentioned measurement result was summarized in Table 1 thru/or 5.

[0063]

[Table 1]

電池	添加剤1		添加剤2		100°C×48時間 放置後	60°C×30日 放置後	
	物質名	添加量 (wt%)	物質名	添加量 (wt%)	電池厚み (mm)	電池厚み (mm)	容量保持率 (%)
実施例1	シクロヘキシルベンゼン	3	1, 3-プロパンスルホン	0.5	8.8	4.9	81
実施例2	シクロヘキシルベンゼン	3	1, 4-ブタンスルホン	0.5	9.0	4.9	89
実施例3	シクロヘキシルベンゼン	3	1, 3-プロパンスルホン	0.5	8.6	4.7	81
実施例4	シクロヘキシルベンゼン	3	グリコールサルフェート	0.5	8.9	4.9	90
実施例5	シクロヘキシルベンゼン	3	プロピレングリコールサルフェート	0.5	9.0	4.9	90
実施例6	シクロヘキシルベンゼン	3	ビニルカーボネート	0.5	9.1	4.8	90
実施例7	シクロヘキシルベンゼン	3	1, 3-プロパンスルホン	1	8.5	4.7	96
実施例8	シクロヘキシルベンゼン	3	1, 4-ブタンスルホン	1	8.6	4.8	93
実施例9	シクロヘキシルベンゼン	3	1, 3-プロパンスルホン	1	8.4	4.6	97
実施例10	シクロヘキシルベンゼン	3	グリコールサルフェート	1	8.6	4.8	94
実施例11	シクロヘキシルベンゼン	3	プロピレングリコールサルフェート	1	9.1	4.8	94
実施例12	シクロヘキシルベンゼン	3	ビニルカーボネート	1	9.1	4.8	93
実施例13	シクロペンチルベンゼン	3	1, 3-プロパンスルホン	1	8.6	4.8	96
実施例14	シクロペンチルベンゼン	3	1, 4-ブタンスルホン	1	8.8	4.8	94
実施例15	シクロペンチルベンゼン	3	1, 3-プロパンスルホン	1	8.6	4.8	97
実施例16	シクロペンチルベンゼン	3	グリコールサルフェート	1	8.6	4.8	95
実施例17	シクロペンチルベンゼン	3	プロピレングリコールサルフェート	1	8.5	4.7	94
実施例18	シクロペンチルベンゼン	3	ビニルカーボネート	1	8.8	4.7	93

[0064]

[Table 2]

電池	添加剤1		添加剤2		100°C×48時間 放置後	60°C×30日 放置後	
	物質名	添加量 (wt%)	物質名	添加量 (wt%)	電池厚み (mm)	電池厚み (mm)	容量保持率 (%)
実施例19	エフェニル	3	1, 3-プロパンスルホン	1	9.3	4.9	93
実施例20	エフェニル	3	1, 4-ブタンスルホン	1	9.5	5.0	92
実施例21	エフェニル	3	1, 3-プロパンスルホン	1	9.3	4.8	94
実施例22	エフェニル	3	グリコールサルフェート	1	9.7	5.0	93
実施例23	エフェニル	3	プロピレングリコールサルフェート	1	9.7	4.9	93
実施例24	エフェニル	3	ビニルカーボネート	1	9.8	4.8	92
実施例25	2-フルオロエフェニル	3	1, 3-プロパンスルホン	1	8.8	4.8	97
実施例26	2-フルオロエフェニル	3	1, 4-ブタンスルホン	1	8.8	4.7	95
実施例27	2-フルオロエフェニル	3	1, 3-プロパンスルホン	1	8.8	4.5	97
実施例28	2-フルオロエフェニル	3	グリコールサルフェート	1	8.8	4.8	96
実施例29	2-フルオロエフェニル	3	プロピレングリコールサルフェート	1	8.8	4.7	96
実施例30	2-フルオロエフェニル	3	ビニルカーボネート	1	9.0	4.5	95

[0065]

[Table 3]

電池	添加剤1		添加剤2		100°C×48時間 放置後	60°C×30日 放置後	
	物質名	添加量 (wt%)	物質名	添加量 (wt%)	電池厚み (mm)	電池厚み (mm)	容量保持率 (%)
実施例31	クメン	3	1, 3-プロパンスルホン	1	8.9	4.8	95
実施例32	クメン	3	1, 4-ブタンスルホン	1	9.0	4.9	94
実施例33	クメン	3	1, 3-プロパンスルホン	1	8.8	4.8	96
実施例34	クメン	3	グリコールサルフェート	1	9.1	4.9	96
実施例35	クメン	3	プロピレングリコールサルフェート	1	9.0	4.8	95
実施例36	クメン	3	ビニルカーボネート	1	9.2	4.7	94
実施例37	1, 3-ジイソプロピルベンゼン	3	1, 3-プロパンスルホン	1	9.1	4.8	95
実施例38	1, 3-ジイソプロピルベンゼン	3	1, 4-ブタンスルホン	1	9.1	4.8	94
実施例39	1, 3-ジイソプロピルベンゼン	3	1, 3-プロパンスルホン	1	9.0	4.8	96
実施例40	1, 3-ジイソプロピルベンゼン	3	グリコールサルフェート	1	9.3	4.9	95
実施例41	1, 3-ジイソプロピルベンゼン	3	プロピレングリコールサルフェート	1	9.3	4.9	95
実施例42	1, 3-ジイソプロピルベンゼン	3	ビニルカーボネート	1	9.3	4.8	94
実施例43	1, 4-ジイソプロピルベンゼン	3	1, 3-プロパンスルホン	1	9.1	4.8	95
実施例44	1, 4-ジイソプロピルベンゼン	3	1, 3-ブタンスルホン	1	9.2	4.8	95
実施例45	1, 4-ジイソプロピルベンゼン	3	1, 3-プロパンスルホン	1	9.0	4.6	96
実施例46	1, 4-ジイソプロピルベンゼン	3	グリコールサルフェート	1	9.5	4.9	96
実施例47	1, 4-ジイソプロピルベンゼン	3	プロピレングリコールサルフェート	1	9.4	4.8	95
実施例48	1, 4-ジイソプロピルベンゼン	3	ビニルカーボネート	1	9.6	4.7	94

[0066]

[Table 4]

電池	添加剤1		添加剤2		100℃×48時間 放置後	60℃×30日 放置後
	物質名	添加量 (wt%)	物質名	添加量 (wt%)	電池厚み (mm)	容量保持率 (%)
実施例49	1-メチルプロピルベンゼン	3	1,3-プロパンスルホン	1	8.9	4.8
実施例50	1-メチルプロピルベンゼン	3	1,4-ブタンスルホン	1	9.0	4.8
実施例51	1-メチルプロピルベンゼン	3	1,3-プロパンスルホン	1	8.8	4.8
実施例52	1-メチルプロピルベンゼン	3	グリコールサルフェート	1	9.1	4.8
実施例53	1-メチルプロピルベンゼン	3	プロピレングリコールサルフェート	1	9.1	4.7
実施例54	1-メチルプロピルベンゼン	3	ビニレンカーボネート	1	8.2	4.8
実施例55	1,3-ビス(1-メチルプロピル)ベンゼン	3	1,3-プロパンスルホン	1	9.1	4.8
実施例56	1,3-ビス(1-メチルプロピル)ベンゼン	3	1,4-ブタンスルホン	1	9.3	4.8
実施例57	1,3-ビス(1-メチルプロピル)ベンゼン	3	1,3-プロパンスルホン	1	9.0	4.8
実施例58	1,3-ビス(1-メチルプロピル)ベンゼン	3	グリコールサルフェート	1	9.5	4.9
実施例59	1,3-ビス(1-メチルプロピル)ベンゼン	3	プロピレングリコールサルフェート	1	9.6	4.9
実施例60	1,3-ビス(1-メチルプロピル)ベンゼン	3	ビニレンカーボネート	1	9.7	4.8
実施例61	1,4-ビス(1-メチルプロピル)ベンゼン	3	1,3-プロパンスルホン	1	9.2	4.8
実施例62	1,4-ビス(1-メチルプロピル)ベンゼン	3	1,4-ブタンスルホン	1	9.1	4.9
実施例63	1,4-ビス(1-メチルプロピル)ベンゼン	3	1,3-プロパンスルホン	1	9.0	4.8
実施例64	1,4-ビス(1-メチルプロピル)ベンゼン	3	グリコールサルフェート	1	9.5	4.9
実施例65	1,4-ビス(1-メチルプロピル)ベンゼン	3	プロピレングリコールサルフェート	1	9.5	4.9
実施例66	1,4-ビス(1-メチルプロピル)ベンゼン	3	ビニレンカーボネート	1	9.5	4.8

[0067]

[Table 5]

電池	添加剤1		添加剤2		100℃×48時間 放置後	60℃×30日 放置後
	物質名	添加量 (wt%)	物質名	添加量 (wt%)	電池厚み (mm)	容量保持率 (%)
比較例 1	なし	—	なし	—	13.1	8.5
比較例 2	シクロヘキシルベンゼン	3	なし	—	10.3	8.2
比較例 3	シクロペンチルベンゼン	3	なし	—	10.4	8.2
比較例 4	ピリニル	3	なし	—	10.3	8.5
比較例 5	2-プロパルジオピラニル	3	なし	—	10.4	8.1
比較例 6	クマセン	3	なし	—	10.6	8.2
比較例 7	1,3-ジニプロピルベンゼン	3	なし	—	10.9	8.3
比較例 8	1,4-ジニプロピルベンゼン	3	なし	—	11.0	8.2
比較例 9	1-メチルプロピルベンゼン	3	なし	—	10.8	8.3
比較例 10	1,3-ビス(1-メチルプロピル)ベンゼン	3	なし	—	10.8	8.3
比較例 11	1,4-ビス(1-メチルプロピル)ベンゼン	3	なし	—	10.9	8.3
比較例 12	なし	—	1,3-プロパンスルホン	1	12.5	5.3
比較例 13	なし	—	1,4-ブタンスルホン	1	12.6	5.4
比較例 14	なし	—	1,3-プロパンスルホン	1	12.3	5.3
比較例 15	なし	—	グリコールサルフェート	1	12.5	5.5
比較例 16	なし	—	プロピレングリコールサルフェート	1	12.5	5.6
比較例 17	なし	—	ビニレンカーボネート	1	12.7	5.5

[0068] When the <result> (cell bulging in 100 **) working examples 1 thru/or 66 were compared with the comparative example 1, in the comparative example 1, it was remarkably [to cell bulging having been 5.8 mm or less in working examples 1 thru/or 66 / as 9.1 mm] large. The comparative example 1 this A sultone compound, cyclic sulfate, vinylene carbonate, The alkylbenzene derivative which has the third class carbon which adjoins a phenyl group, As a result of not forming a film good on a cathode and an anode by not including a cycloalkyl benzene derivative and a biphenyl derivative at all, it is thought that it is because the cell blistered for the gas emitted by disassembly of the electrolysis solution.

[0069] When the working examples 1 thru/or 66 were compared with the comparative examples 2 thru/or 11, in the comparative examples 2 thru/or 11, cell bulging was large compared with not less than 6.3 mm and the working examples 1 thru/or 66. This is considered to be based on the following Reasons. In a sultone compound, cyclic sulfate, and the comparative examples 2 thru/or 11 that do not contain vinylene carbonate, a good film is not formed on an anode. For this reason, generating of methane on an anode, etc. cannot be controlled at the time of an elevated temperature. Therefore, also in 100 **, bulging of a cell becomes large with the methane emitted on an anode etc.

[0070] Also in the comparative examples 2 thru/or 11, since the film is formed on the cathode like the working examples 1 thru/or 66, carbon dioxide generating from the cathode which is the main cause of cell bulging is considered to be controlled. However, although it does not result in generating of carbon dioxide on the cathode covered with the film, it is thought that the partial decomposition reaction of an electrolysis solution

is advancing. It is thought that the substance in which some electrolysis solutions were disassembled generates by such a decomposition reaction. Thus, it is thought that the substance in which some electrolysis solutions were disassembled decomposes further on an anode, and generates methane etc. In the working examples 1 thru/or 66, since the film is formed also on the anode, the above reactions are also inhibited.

[0071]When the working examples 1 thru/or 66 were compared with the comparative examples 12 thru/or 17, in the comparative examples 12 thru/or 17, cell bulging was large compared with not less than 8.3 mm and the working examples 1 thru/or 66. This is considered to be based on the following Reasons. In the comparative examples 12 thru/or 17 which do not contain the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group, a good film is not formed on a cathode. For this reason, generating of the carbon dioxide on a cathode cannot be controlled at the time of an elevated temperature. Therefore, in 100 ** neglect, a cell will blister with the carbon dioxide emitted on a cathode.

[0072]Also in the comparative examples 12 thru/or 17, since the film is formed on the anode like the working examples 1 thru/or 66, it is thought that generating of methane from an anode, etc. is controlled. However, although it does not result in generating of methane etc. on the anode covered with the film, it is thought that the partial decomposition reaction of an electrolysis solution is advancing. It is thought that the substance in which some electrolysis solutions were disassembled generates by such a decomposition reaction. Thus, it is thought that the substance in which some electrolysis solutions were disassembled decomposes further on a cathode, and generates carbon dioxide etc. In the working examples 1 thru/or 66, since the film is formed also on the cathode, the above reactions are also inhibited.

[0073]As shown in Table 1, the above-mentioned result and the same result were obtained also about cell bulging after the long-term neglect at 60 **. As the capacitance retention after the long-term neglect at 60 ** was shown in a mist beam and Table 1, the above-mentioned result and the result of the same tendency were obtained.

[0074](Conclusion) That it is few as nonaqueous electrolyte is chosen from a sultone compound, cyclic sulfate, and vinylene carbonate As mentioned above, a kind, By [which contain a kind at least] being chosen out of the alkylbenzene derivative, cycloalkyl benzene derivative, and biphenyl derivative which have the third class carbon which adjoins a phenyl group showed that the nonaqueous secondary battery provided with the outstanding elevated-temperature neglect characteristic could be obtained.

[0075]<Other embodiments> this invention is not limited to the embodiment described with the above-mentioned description and Drawings, and further, within limits which do not deviate from a summary besides the following, it can be contained in technical scope of this invention, and the following embodiments can also be changed variously, and can carry it out, for example.

[0076]In the above-mentioned embodiment, although explained as the square-shaped nonaqueous secondary battery 1, battery structure in particular is not limited but, of course, it is good also as a cylindrical shape, saccate, a lithium-polymer battery, etc.

[0077]

[Effect of the Invention]According to this invention, the nonaqueous secondary battery provided with the outstanding elevated-temperature neglect characteristic can be obtained.

[Translation done.]